

Challenges in Understanding and Development of Predictive Models of Plasma Assisted Combustion

Igor V. Adamovich and Walter R. Lempert

*Nonequilibrium Thermodynamics Laboratory
Department of Mechanical and Aerospace Engineering
The Ohio State University, Columbus, OH 43210*

Abstract

Key challenges to quantitative insight into fuel-air plasma kinetics, as well as plasma assisted ignition and flameholding, are identified and assessed based on the results of recent experimental and kinetic modeling studies. Experimental and modeling approaches to address these critical issues are discussed. The results have major implications for fundamental understanding of pulsed electric discharge dynamics, molecular energy transfer in reacting flows, plasma chemical reactions, and development of low-temperature plasma assisted combustion technologies.

Report Documentation Page			Form Approved OMB No. 0704-0188	
<p>Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.</p>				
1. REPORT DATE 2014	2. REPORT TYPE	3. DATES COVERED 00-00-2014 to 00-00-2014		
4. TITLE AND SUBTITLE Challenges in Understanding and Development of Predictive Models of Plasma Assisted Combustion			5a. CONTRACT NUMBER	
			5b. GRANT NUMBER	
			5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)			5d. PROJECT NUMBER	
			5e. TASK NUMBER	
			5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Ohio State University, Department of Mechanical and Aerospace Engineering, 201 W. 19th Ave, Columbus, OH, 43210			8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)			10. SPONSOR/MONITOR'S ACRONYM(S)	
			11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited				
13. SUPPLEMENTARY NOTES accepted for publication in Plasma Physics and Controlled Fusion, 2014.				
14. ABSTRACT Key challenges to quantitative insight into fuel-air plasma kinetics, as well as plasma assisted ignition and flameholding, are identified and assessed based on the results of recent experimental and kinetic modeling studies. Experimental and modeling approaches to address these critical issues are discussed. The results have major implications for fundamental understanding of pulsed electric discharge dynamics, molecular energy transfer in reacting flows, plasma chemical reactions, and development of low-temperature plasma assisted combustion technologies.				
15. SUBJECT TERMS				
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Same as Report (SAR)	18. NUMBER OF PAGES 14
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified		
19a. NAME OF RESPONSIBLE PERSON				

1. Introduction

Over the last 10-15 years, there has been significant progress demonstrating the utility of non-equilibrium plasmas for augmentation of combustion phenomena, such as reduction of ignition delay time and ignition temperature, as well as increase in flame stability and flammability limits [1,2]. High peak voltage, nanosecond pulse duration discharges are of particular interest for plasma assisted combustion since they can generate diffuse nonequilibrium plasmas at high pressures (~ 1 bar) and high pulse repetition rates (up to ~ 100 kHz), and are characterized by high peak reduced electric fields, E/N , of several hundred Townsend (1 Td = 10^{-17} V·cm 2). At these high E/N values, a significant fraction of discharge input energy goes into population of excited states of molecules (vibrational and electronic), as well as molecular dissociation and ionization by electron impact. Collisional quenching of the excited states (including reactive quenching) and reactions of radical species generated in the discharge considerably expand the variety of chemical reactions in low-temperature fuel-air mixtures, resulting in fuel oxidation and ignition. From a fundamental kinetics perspective, however, the dominant energy transfer and chemical reaction processes in these plasmas remain not fully understood, especially when fairly complex hydrocarbon fuels are involved. Without such understanding, predictive kinetic modeling and analysis of plasma assisted combustion phenomena remains problematic. The main objective of the present work is to identify and assess most significant challenges to quantitative insight into fuel-air plasma kinetics, as well as plasma assisted ignition and flameholding, based on the results of recent experimental and modeling studies.

2. Electric field and electron density: measurements and prediction

It is well known that energy partition among different energy modes in nonequilibrium, low-temperature, high-pressure plasmas (rotational, vibrational, electronic, dissociation, and ionization) is controlled primarily by the electron energy distribution function. Over a wide range of conditions, this partition can be characterized in terms of the reduced electric field, E/N . Electron density, n_e , is the other parameter that controls energy coupling to the plasma, such that specific power loading is proportional to the product of E/N and n_e . Thus, knowledge of these two key parameters is critical for insight into kinetics of energy transfer and chemical reactions in these plasmas. Estimating E/N and n_e in the plasma from discharge voltage and current waveforms, especially in transient discharges that develop as ionization waves, may well result in significant uncertainties in predicting other plasma parameters, such as vibrational and electronic excitation, e.g. $N_2(X^1\Sigma, v=0) + e \rightarrow N_2(X^1\Sigma, v>0, A^3\Sigma, B^3\Pi, C^3\Pi) + e$, as well as molecular dissociation by electron impact, e.g. $O_2(X^1\Sigma) + e \rightarrow O(^3P, ^1D) + O(^3P) + e$. Thus, measurements of electric field, electron density, and electron temperature in transient plasmas sustained by nanosecond pulse duration discharges, and their comparison with modeling predictions, are critical for fuel-air plasma characterization and validation of kinetic models. Truly predictive models should incorporate, at the very least, realistic electrode geometry, Poisson equation for the electric field, and equations for number densities of charges species (e.g. see [3,4]), such that electric field and electron density distributions in the plasma could be predicted based on the experimental voltage waveform, and compared with the experimental results.

Four-wave mixing / CARS and Thomson scattering are two powerful laser diagnostics used recently for time-resolved electric field measurements [5-7], as well as time-resolved electron density and electron temperature measurements [8-10] in high-pressure, high specific energy loading molecular plasmas. Electric field measurements have been performed using both H₂ and N₂ as the active species, which are among the dominant species in plasma-assisted combustion environments. Sub-nanosecond time resolution electric field diagnostics are under

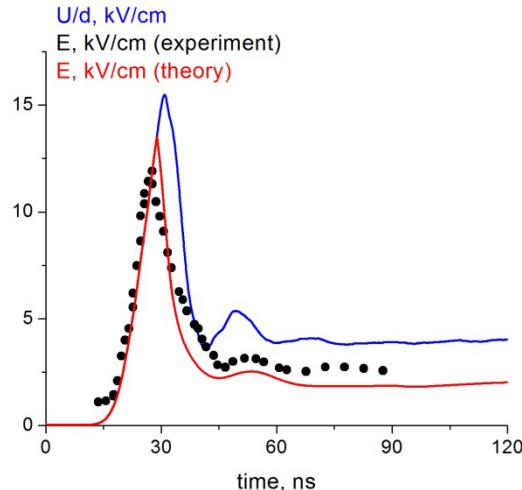


Figure 1. Experimental [6] and predicted electric field and applied voltage / electrode gap in a ns pulse, plane-to-plane discharge in N₂ at 0.25 bar, electrode gap of 1.2 mm.

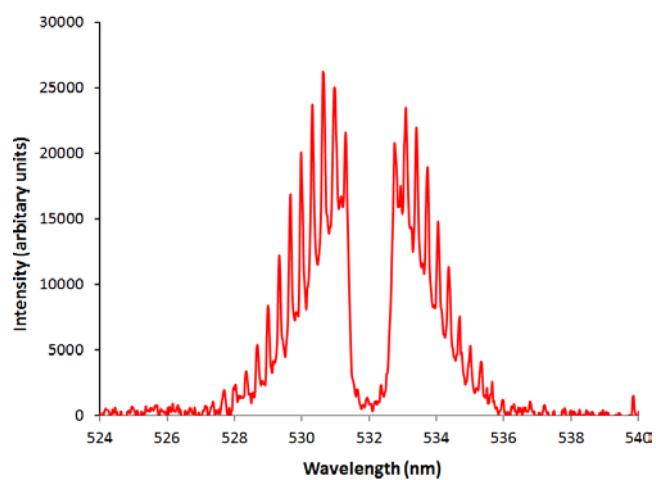


Figure 2. Thomson / Raman scattering spectrum in a 10% O₂-He mixture at 100 Torr, 100 ns after ns pulse discharge current rise. Distance between spherical electrodes 1 cm. $n_e = 6 \cdot 10^{13} \text{ cm}^{-3}$, $T_e = 1.7 \text{ eV}$ [10].

development [7]. Figure 1 compares experimental [6] and predicted electric field in nanosecond pulse discharge in nitrogen at 0.25 bar, using the kinetic model developed in Ref. [11]. Rapid electric field reduction during breakdown and the effect of cathode voltage fall on the field in the plasma after breakdown (such that the field is significantly lower compared to the ratio of voltage over distance) are readily apparent. Thomson scattering electron density measurements in molecular plasmas are quite challenging because of strong Rayleigh and Raman scattering [8]; however, Rayleigh scattering can be filtered out using a mask in a triple-grating spectrometer, and Raman spectrum can be subtracted if signal-to-noise and spectral resolution are sufficiently high [8]. Figure 2 plots a typical Thomson / Raman scattering spectrum in a 10% O₂-He mixture at 100 torr, 100 ns after the beginning of the discharge pulse. The gap in the center of the spectrum, caused by blocking of Rayleigh scattering, and Raman lines of O₂ are apparent. The inferred electron density and electron temperature at these conditions are $n_e = 6 \cdot 10^{13} \text{ cm}^{-3}$ and $T_e = 1.7 \text{ eV}$.

3. Temperature and vibrational level populations: measurements and prediction

The parameter that has the most significant effect on chemical processes in fuel-air plasmas, in particular on the rates of chain branching fuel oxidation reactions, is gas temperature. Therefore time-resolved and spatially-resolved temperature measurements in these plasmas, as well as comparison with kinetic modeling predictions, are extremely important for understanding the mechanism of plasma assisted ignition. Since in molecular plasmas a significant fraction of discharge energy is loaded into the vibrational mode of nitrogen, with subsequent vibrational relaxation, time-resolved and spatially-resolved measurements of N₂ vibrational temperature and vibrational level populations are also critical for predicting the rate of energy thermalization in the plasma. Recently, these measurements have become available due to progress in development of picosecond CARS [12] and spontaneous Raman scattering laser diagnostics [13]. As expected, O₂ vibrational excitation is much less pronounced compared to that of N₂ [13].

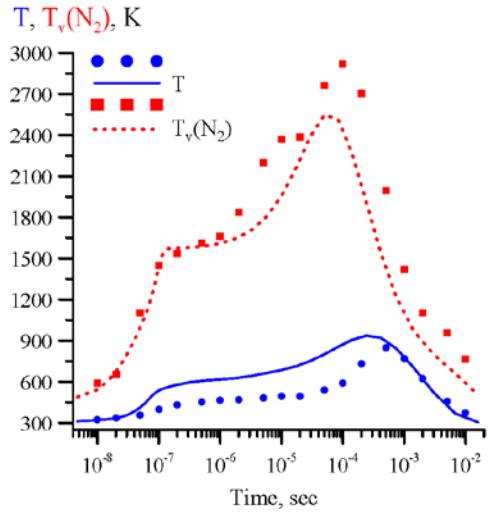


Figure 3. Experimental and predicted temperature and N₂ vibrational temperature during and after a ns pulse discharge in air between two spherical electrodes 1 cm apart at 100 Torr [12].

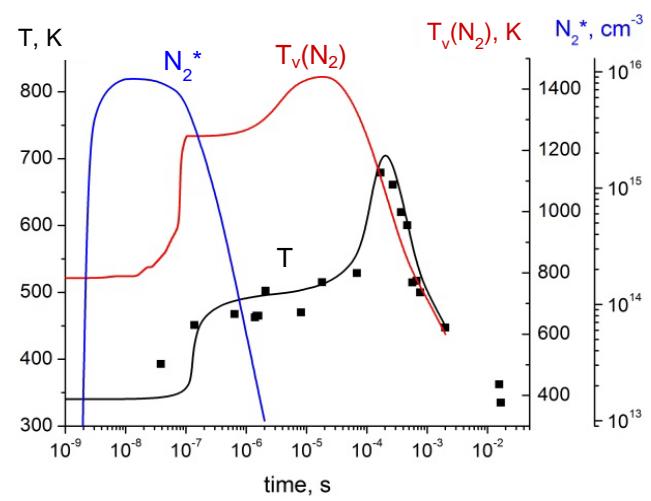


Figure 4. Experimental and predicted temperature during and after a ns discharge pulse in an H₂-air mixture ($\phi=0.14$) between two spherical electrodes 0.9 cm apart at 40 Torr, plotted together with predicted number density of electronically excited N₂ molecules and $T_v(N_2)$.

Figure 3 plots experimental (ps CARS) and predicted, time-resolved rotational/translational temperature and “first level” N_2 vibrational temperature, $T_v = \omega_e(1 - 2x_e)/\ln(N_{v=0}/N_{v=1})$, during and after ~ 100 ns duration discharge pulse in air, at 100 Torr [12]. “Rapid” temperature rise, on a short time scale, $t \sim 10^{-7}$ s – 10^{-6} s, up to $T \sim 500$ K (somewhat difficult to see in Fig. 3), is primarily due to energy release during quenching of excited electronic states of nitrogen, $N_2(A^3\Sigma, B^3\Pi, C^3\Pi) + O_2 \rightarrow N_2(X^1\Sigma) + O + O$. It has been predicted by kinetic modeling [14] and has also been studied by optical emission spectroscopy in nanosecond pulse discharges at atmospheric pressure [15]. From Fig. 3, it can be seen that the discharge produces significant vibrational nonequilibrium, $T_{v,max} \sim 2900$ K, $T_{max} \sim 850$ K. In these experiments, $N_2(v=0-9)$ vibrational level populations have also been measured, indicating strongly non-Boltzmann, “bimodal” vibrational distribution [12]. Kinetic modeling calculations [12] demonstrated that significant transient rise of N_2 vibrational temperature after the discharge pulse (from $T_{v,max} \sim 1500$ K to ~ 2900 K at $t \sim 10^{-7}$ s – 10^{-4} s, see Fig. 3) is due to “downward” vibration-vibration energy exchange, $N_2(v=2) + N_2(v=0) \rightarrow N_2(v=1) + N_2(v=1)$. T_v reduction at $t \sim 10^{-4}$ s – 10^{-3} s, which coincides with significant “slow” temperature rise on the same time scale, from $T \sim 500$ K to ~ 850 K, is due to vibration-translation relaxation of N_2 by O atoms, $N_2(v) + O \rightarrow N_2(v-1) + O$. Obviously, both “rapid” and “slow” temperature increase, caused by quenching of excited electronic states and vibrational relaxation of nitrogen, respectively, have significant effect on the energy balance and thus are critically important for the rates of fuel oxidation in nanosecond pulse fuel-air plasmas.

The effect of “rapid” heating in nanosecond pulse fuel-air plasmas is illustrated in greater detail in Fig. 4, which compares experimental (ps pure rotational CARS) and predicted (using the kinetic model developed in Ref. [11]) temperatures during and after a nanosecond pulse discharge in an H_2 -air mixture at 40 Torr. It can be seen that time scales for the “rapid” temperature rise and decay of electronically excited N_2 molecules are the same (the “slow” rise is due to N_2 vibrational relaxation by O atoms). “Rapid” heating becomes considerably more pronounced at higher pressures [15], both due to higher specific energy loading in a localized discharge filament and due to faster quenching of excited electronic states of N_2 . This raises the following questions: can plasma chemical reactions among excited electronic species and radicals generated in the low-temperature plasma compete with “conventional” fuel-air chemical reactions, the rates of which rapidly increase with temperature? At what pressures does “rapid” heating become the dominant effect in transient fuel-air plasmas, compared to low-temperature excited species and radical species chemistry? Answering these questions would have considerable impact on development of plasma-assisted combustion applications. This requires additional systematic studies in well characterized fuel-air plasmas, over a wide range of pressures, as well as comparison with kinetic modeling calculations to evaluate contributions of different mechanisms.

4. Effect of excited species and radicals on plasma chemistry

Reactive quenching of excited electronic states and vibrational relaxation in air and fuel-air mixtures may have a significant effect on plasma chemistry, generating radicals such as O, H, and OH, e.g. $O(^1D) + H_2 \rightarrow H + OH$, and dissociating oxygen and fuel species, e.g. $N_2(A^3\Sigma, B^3\Pi, C^3\Pi) + H_2 \rightarrow N_2(X^1\Sigma) + H + H$, $N_2(A^3\Sigma, B^3\Pi, C^3\Pi) + O_2 \rightarrow N_2(X^1\Sigma) + O + O$. Plasma-generated radicals can initiate fuel oxidation chain reactions, such as $H + O_2 \rightarrow OH + O$, $O + H_2 \rightarrow OH + H$, and generate nitric oxide, $N_2^* + O \rightarrow NO + N$ (here the asterisk stands for N_2

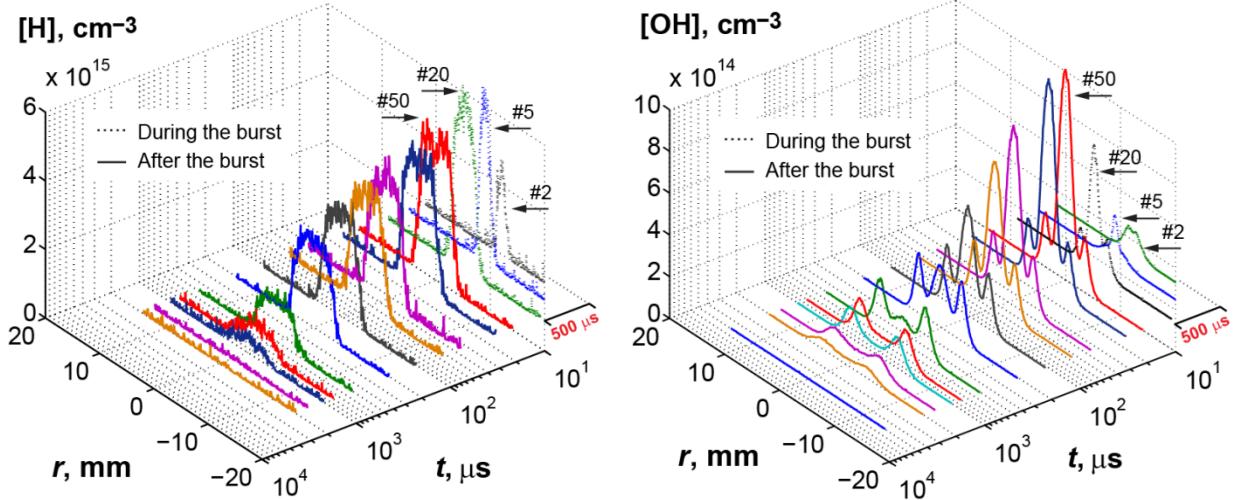


Figure 5. Radial distributions of absolute $[H]$ (left) and $[OH]$ (right) across a point-to-point discharge filament during and after ns discharge burst (50 pulses) in a $\text{Ar}:O_2:\text{H}_2 = 80:20:2$ mixtures at $P=40$ torr and $T_0 = 300$ K [19]. Pulse numbers are indicated in the figure.

excited electronic or vibrational states), which may strongly affect radical concentrations. For this reason, absolute measurements of electronically excited (by Cavity Ring-Down Spectroscopy and calibrated optical emission spectroscopy [16]) and vibrationally excited N_2 molecules (by CARS [12] or spontaneous Raman scattering [13]) as well as of N , O , NO , H , and OH radicals (by Single-Photon and Two-Photon Absorption LIF [16-18]) in transient fuel-air plasmas yield critical insight into kinetics of chemical reactions of plasma-generated radicals. Spatially-resolved LIF, TALIF, and Rayleigh scattering measurements in transient plasmas with strong gradients [19] are especially desirable (see Fig. 5). Figure 6 compares experimental (LIF and TALIF) [18] and predicted [11] time-resolved absolute number densities of O , N , and NO after a ns pulse discharge in air at 100 Torr, at low pulse energy, near-room temperature conditions. In these experiments, $N_2(v=0-4)$ populations have also been measured, by ps CARS. The results of these measurements demonstrated that (i) vibrationally excited $N_2(X^1\Sigma, v)$ molecules do not have a detectable effect on NO formation in ns pulse low-temperature air plasmas, and (ii) NO at these conditions is formed primarily by reactive quenching of a number of excited electronic states of N_2 , including multiple singlet and triplet states.

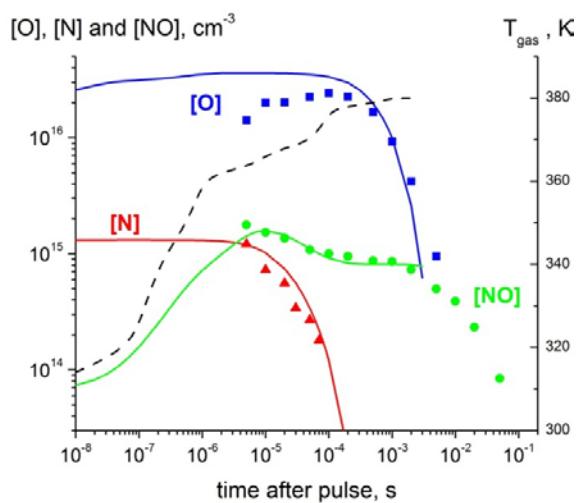


Figure 6. Experimental and predicted absolute O , N , and NO number densities after a ns pulse discharge in air between two spherical electrodes 1 cm apart at 100 Torr (low pulse energy, near-room temperature conditions).

The effect of vibrationally excited nitrogen molecules, $N_2(X^1\Sigma,v)$, on plasma chemical reactions have been discussed in the literature for quite some time. In fact, one of the objectives of simultaneous ps CARS, LIF, and TALIF measurements [18] was to quantify the effect of $N_2(X^1\Sigma,v) + O \rightarrow NO + N$ reaction on the rate of NO formation in low-temperature transient air plasmas. However, the contribution of this reaction, compared to reactive quenching of excited electronic states of N_2 appears to be small. This result does not imply that $N_2(X^1\Sigma,v)$ molecules cannot affect air and fuel-air plasma chemical reactions in general. Recent time-resolved measurements of [OH] in nanosecond pulse discharge afterglow in preheated hydrocarbon-air mixtures [20], which demonstrated anomalously long OH lifetime, led the authors to suggest that vibrationally excited nitrogen may delay OH recombination due to near-resonance energy transfer to HO₂ radical, $N_2(X^1\Sigma,v=1) + HO_2 \rightarrow N_2(X^1\Sigma,v=0) + HO_2$ (v_2+v_3) $\rightarrow N_2 + H + O_2$ [21]. However, gas temperature and N_2 vibrational temperature in these experiments have not been measured, such that a more direct effect of heating the flow by the discharge on OH lifetime cannot be ruled out. Direct vibrational temperature measurements are critical due to significant uncertainty in state-specific rates of N_2 vibrational relaxation in reacting fuel-air mixtures. It may well be possible that reactions of vibrationally excited N_2 molecules in fuel-air plasmas may affect low-temperature fuel oxidation chemistry, and additional experimental studies (such as simultaneous N_2 vibrational CARS and OH LIF measurements) are needed to verify this hypothesis.

A closely related issue is the effect of long-lived metastable species generated in molecular plasmas, such as $O_2(a^1\Delta)$, on fuel-oxidizer plasma chemistry, compared to radicals participating in rapid reactions of fuel oxidation, such as O, H, and OH. Recent experiments show that metastable $O_2(a^1\Delta)$ molecules, which have a long lifetime and may accumulate in O₂-containing plasmas up to mole fractions of several per cent, have a significant effect on H₂-O₂ ignition delay length [22] and on C₂H₄-O₂-Ar flame speed [23]. In Refs. [23,24], the effect of $O_2(a^1\Delta)$ was isolated from that of O atoms and ozone (which serves a source of O and H radicals in the flame preheat zone). However, predictive capability of kinetic models is limited by lack of data on collisional quenching of $O_2(a^1\Delta)$ by radicals and hydrocarbon species [24,25]. On the other hand, the effect of O atoms on CH₄ and C₂H₄ oxidation in low-temperature plasmas [26-28], as well as on extinction limit of low-pressure CH₄ diffusion flames [28,29], appears to be relatively well understood. In particular, at temperatures far below ignition threshold radical species generated in the plasma predominantly recombine and do not result in ignition, due to near absence of chain branching processes.

Finally, the effect of low-temperature plasma-generated radicals on low octane number fuels exhibiting cool flame chemistry vs. high octane number fuels, for which cool flames are not observed, is not understood and requires further experimental and modeling studies. At temperatures below the self-ignition temperature, plasma-generated O atoms (as well as other radical or excited species) enhance alkyl radical (R) production (e.g. $RH + O \rightarrow R + OH$). The subsequent fate of the alkyl radical determines whether cool flame chemistry will occur or not [30,31]. At high temperatures, the alkyl radical thermally decomposes to form smaller hydrocarbons, delaying significant radical branching and heat release until later in the reaction sequence and, more importantly, higher temperatures. At low temperatures, the alkyl radical may form the alkylperoxy radical by reacting with molecular oxygen ($R + O_2 \rightarrow RO_2$). The stabilization of RO_2 , followed by internal isomerization to form the hydroperoxyalkyl radical ($QOOH$), and addition of a second O₂ molecule to form O_2QOOH , results in significant radical branching during the decomposition and further reactions of O_2QOOH . Enhancing this low-

temperature cool flame sequence, and enabling it over a broader range of conditions, is desirable for shortening ignition delays of large hydrocarbon fuels. The molecular structure of the fuel, which affects octane number, influences the rates of R and $QOOH$ formation, and how these processes are altered by the plasma chemistry requires further study [32]. The role of $O_2(a^1\Delta)$ is of particular uncertainty in this low temperature reaction sequence.

5. Development of predictive plasma assisted ignition / combustion chemistry mechanism

Quantitative predictions of ignition by low-temperature plasmas requires knowledge of rates of molecular energy transfer processes, such as electron impact excitation and dissociation of air and fuel species, vibrational relaxation, rates and products of reactive quenching of excited electronic states, reactions among charged species, as well as a mechanism of fuel oxidation via “conventional” chemical reactions at low temperatures. Kinetic mechanisms of “conventional” combustion [33,34] have been developed and validated for high temperature conditions and may well be inapplicable at low temperatures typical for many plasma assisted combustion environments. An illustration of this is found in a recent study [17] which compares absolute time-resolved $[OH]$ and temperature measurements by LIF in lean H_2 -air and hydrocarbon-air mixtures excited by a burst of nanosecond discharge pulses with kinetic modeling calculations, using conventional hydrocarbon-air combustion mechanisms. Although modeling predictions for H_2 -air, CH_4 -air, and C_2H_4 -air agree with the data fairly well [17], the agreement between the model and the data in C_3H_8 -air is quite poor. This demonstrates the need for development of an accurate, predictive plasma assisted combustion chemistry mechanism. Predictive capability of a plasma chemistry model involving such a large number of energy transfer processes and reactions requires extensive, preferably built-in, kinetic sensitivity analysis to identify the dominant processes. Identifying the reduced reaction mechanism is extremely critical, especially for hydrocarbons, since kinetic modeling of coupled ns pulse discharge dynamics, energy transfer in the plasma, and plasma assisted combustion requires incorporating a wide range of time scales, $\sim 10^{-12}$ s – 10^{-2} s, and is very computationally intensive even in 1-D geometry [35].

Experimental validation of such a mechanism would require comparison with results of plasma assisted ignition experiments at well-characterized conditions, using metrics that would be sufficiently sensitive to kinetics used. The metrics used in conventional combustion kinetics include laminar flame speed, as well as ignition delay time (e.g. measured in a shock tubes or a rapid compression machine). In low-temperature plasma-assisted ignition, these metrics are clearly insufficient since they also need to be correlated with measurements of parameters controlling both plasma chemistry and conventional chemistry reactions, such as as number densities of key radical species and temperature in the plasma. Since species number density measurements using laser diagnostics require significant signal accumulation, this requires the use of well-reproduced, repetitively pulsed plasma ignition cycles [36]. Time-resolved temperature, N_2 vibrational temperature (in case of significant vibrational nonequilibrium), key radical species (such as OH , O , or H), and at least one key dominant species (such as fuel or O_2) measurements during plasma-induced ignition (as illustrated in Fig. 7), appear to provide sufficient amount of data for kinetic mechanism validation. Systematic validation would require doing these measurements over a range of equivalence ratios, fuels, pressures, and energy coupled to the plasma (e.g. number of discharge pulses). Note that single-shot ignition delay time

or ignition temperature measurements, such that obtained in a shock tube or a rapid compression machine, do not lend themselves for time-resolved temperature and species number density measurements.

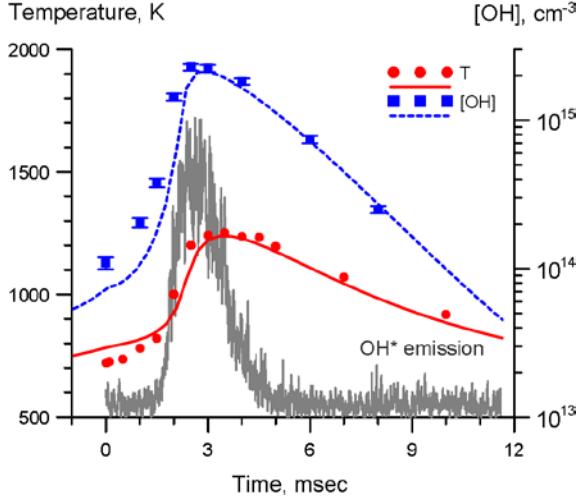


Figure 7. Experimental and predicted temperature and $[OH]$ during ignition after a ns discharge burst in plane-to-plane geometry. H_2 -air, $T_0=500$ K, $P=80$ Torr, $\phi=0.4$, 115 pulses [36]. Temperature and $T_v(N_2)$ are measured by ps CARS at $P=92$ torr, 120 pulses [17].

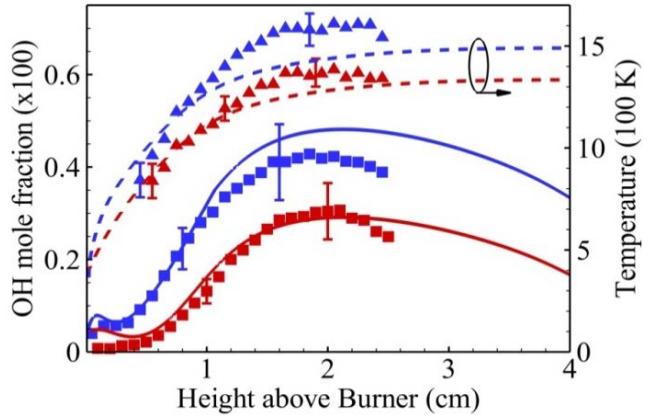


Figure 8. Experimental [37] and predicted [38] temperature and $[OH]$ distributions across a burner stabilized H_2 - O_2 - N_2 flat flame ($\phi=0.5$, $P=25$ Torr), with (blue) and without (red) ns discharge burst (200 pulses) in plane-to-plane geometry. Squares and solid lines: $[OH]$, triangles and dashed lines: temperature.

An approach complementary to time-resolved measurements during repetitively pulsed ignition cycles could be spatially resolved measurements of temperature and species number densities across a premixed or diffusion laminar flame front, at the conditions when radical species are generated by the plasma. These experiments would not require achieving well-reproduced repetitive ignition, which requires operation at very low discharge burst repetition rate, ~1 Hz, to remove combustion products from the test cell [36]. An example of these measurements (by OH LIF [37]), along with modeling calculations, is illustrated in Fig. 8 [38]. Note that the effect of the plasma on flame speed and reaction zone location appears to be relatively modest [23,24,37], and as such is unlikely to be a good metric for kinetic mechanism validation. On the other hand, measurements of radical species and temperature distributions in the preheat zone of the flame, especially at fuel-lean conditions when the effect of plasma is most pronounced [37], may well be used for this purpose.

6. Effect of plasmas on non-premixed turbulent flames and reacting compressible flows

The effect of radical generation in nanosecond pulse discharge plasmas on blow-off velocity and lean flammability limits in premixed and jet diffusion flames has been studied fairly extensively [39,40], demonstrating stable combustion and flameholding at significantly higher velocities and lower equivalence ratios compared to baseline. Recent experiments also provided insight into the temporal response of a lean, premixed, weakly turbulent flame to nanosecond pulse discharge excitation [41], suggesting that the plasma may help control combustion instabilities, such as coupling between heat release and acoustic oscillations. However, the effect of plasmas on non-premixed turbulent flames at high Reynolds numbers remains to be explored.

In these flames, the presence of plasma may help prevent local extinction and/or accelerate re-ignition by producing a pool of radicals at the locations where the local temperature and reaction rates become too low to sustain combustion, due to the flow field turbulence and its interaction with finite-rate chemistry. Additional work in this field, using quantitative laser diagnostics to measure flow field velocity and scalars in turbulent flames in the presence of nonequilibrium plasma is critical. In particular, high-frame rate (~ 10 kHz) turbulent flame imaging of velocity, temperature and species concentrations (e.g. particle imaging velocimetry [42], OH PLIF [42], Rayleigh scattering [43], Raman scattering [44], CH PLIF [45], and CH₂O PLIF [46]), is necessary to begin to understand the coupling between plasma kinetics and turbulent combustion dynamics.

One of the most critical issues of plasma assisted ignition, combustion, and flameholding in non-premixed high-speed flows is whether the plasma needs to be located in the airflow, in fuel injection flow, or in a partially premixed region near the fuel injector. Since mole fractions of hydrocarbon fuels in the mixture are typically fairly low, a few percent (even at stoichiometric conditions), it appears that plasma excitation of airflow and generation of sufficient amounts of excited electronic species and radicals, N₂^{*} and O atoms, would be the obvious approach. However, excitation of airflow upstream of the fuel injection port may result in significant loss of excited species and radicals, both due to quenching and recombination and due to mixing with unexcited air, thus diluting the radical pool. A similar problem exists with plasma excitation of a partially premixed fuel-air region in the vicinity of a fuel injector [47,48]. Since rapid mixing of fuel and airflow is critical for stable combustion, the radicals generated in the discharge may also be significantly diluted in the flow, thus reducing the impact of plasma excitation. A recently suggested approach [49] is to sustain the discharge partially in the fuel injection line and terminate the current path in the combustor, such that the discharge filament would penetrate into the flow with the fuel jet. The advantages of this approach include (i) radical generation in high-speed fuel injection flow and their rapid transport into the airflow; (ii) discharge following a high-speed fuel jet and thus penetrating deep into the airflow; and (iii) fuel-air mixing enhancement. Simple analysis of high electron density plasmas in a high-speed flow [49], such that local ionization / recombination balance is not affected by convection, demonstrates that a steady-state discharge filament may exist only if the current vector is parallel to the flow velocity vector in the filament, $\vec{j} \parallel \vec{u}$. Recently, it has also been demonstrated that fuel-air mixing can be enhanced significantly by unsteady oscillating discharge filaments [50]. Additional studies, both experimental and coupled electric discharge / reacting compressible flow modeling, are necessary to obtain quantitative insight into discharge behavior in high-speed compressible flows, and its effect on ignition and flameholding.

Finally, one of the least explored problems in non-premixed, high-speed compressible flows is the effect of plasma-assisted ignition on combustion instability development. Evidence of such instability, caused by strong coupling between pressure in the combustor and discharge parameters (voltage and current), and resulting in high-amplitude oscillations of pressure and flame front, was detected in recent supersonic combustion experiments [48]. A systematic experimental study of this coupling is necessary to obtain insight into the instability development mechanism, and possibly to control and suppress it.

7. Summary

An overview of recent experimental and kinetic modeling studies of low-temperature plasma-assisted combustion exhibits the following key challenges:

- (i) Measurements and modeling predictions of electric field, electron density, gas temperature, and N₂ vibrational level populations in high-pressure pulsed fuel-air plasmas are necessary for predictive insight into discharge energy partition.
- (ii) Measurements and modeling predictions of excited electronic states of N₂^{*} and key radicals (O, H, OH, and NO) are critical for quantifying their effect on pulsed fuel-air plasma chemistry, including fuels exhibiting cool flame chemistry.
- (iii) Development of predictive plasma assisted combustion chemistry mechanism requires a set of temperature, N₂ vibrational temperature, and radical concentrations data during a repetitively pulsed plasma-enhanced ignition process, or across a pulsed plasma-enhanced flame. The results would help quantify the effect of “rapid” heating, and possibly reactions of vibrationally excited molecules, compared to reactions of plasma-generated radicals.
- (iv) Kinetic sensitivity analysis is necessary to identify the reduced reaction mechanism, which can be incorporated into a practical discharge dynamics / energy transfer / plasma chemistry kinetic model incorporating a wide range of time scales and a realistic geometry.
- (v) Effect of plasmas on non-premixed turbulent flames needs to be studied using high frame rate imaging of temperature and radical species concentrations fields.
- (vi) Electric discharge dynamics and combustion instability development in reacting compressible flows need to be studied experimentally and using a coupled electric discharge / reacting compressible flow modeling.

Acknowledgements

This work has been supported by the U.S. Air Force Office of Scientific Research MURI “Fundamental Aspects of Plasma Assisted Combustion”, Technical Monitor Dr. Chiping Li. The authors would also like to thank R. Yetter, J. Sutton, S. Leonov, N. Popov, and N. Aleksandrov for extensive technical discussions.

References

1. S.M. Starikovskaia, Journal of Physics D: Applied Physics 39 (2006) R265
2. A. Starikovskiy and N. Aleksandrov, Progress in Energy and Combustion Science 39 (2013) 61
3. F. Tholin, D.A. Lacoste, and A. Bourdon, Combustion and Flame 161 (2014) 1235
4. H. Takana and H. Nishiyama, Plasma Sources Science and Technology 23 (2014) 034001
5. T. Ito, K. Kobayashi, U. Czarnetzki, and S. Hamaguchi, Journal of Physics D: Applied Physics, 43 (2010) 062001
6. P. Boehm, D. Luggenhoelscher, and U. Czarnetzki, “Laser-spectroscopic electric field

measurements in a ns-pulsed microplasma in nitrogen”, 66th Annual Gaseous Electronics Conference, October 2013, Princeton, NJ, USA

7. B. Goldberg, S. O’Byrne, and W.R. Lempert, AIAA Paper 2012-0240, 50th AIAA Aerospace Sciences Meeting, January 2012, Nashville, TN, USA
8. A.F.H. van Gessel, E.A.D. Carbone, P.J. Bruggeman, J.J.A.M. van der Mullen, Plasma Sources Science and Technology, 21 (2012) 015003
9. B. van Gessel, R. Brandenburg, and P. Bruggeman, Applied Physics Letters, 103 (2013) 064103
10. A. Roettgen, I.V. Adamovich, and W.R. Lempert, AIAA Paper 2014-2113, 45th AIAA Plasmadynamics and Lasers Conference, June 2014, Atlanta, GA, USA
11. I. Shkurenkov, D. Burnette, W.R. Lempert, and I.V. Adamovich, ”Kinetics of Excited States and Radicals in a Nanosecond Pulse Discharge and Afterglow in Nitrogen and Air”, accepted for publication in Plasma Sources Science and Technology, 2014
12. A. Montello, Z. Yin, D. Burnette, I.V. Adamovich, and W.R Lempert, Journal of Physics D: Applied Physics 46 (2013) 464002
13. A. Lo, G. Cléon, P. Vervisch, and A. Cessou, Applied Physics B: Laser and Optics 107 (2012) 229
14. N. A. Popov, Plasma Physics Reports 27 (2001) 886
15. D.L. Rusterholtz, D.A. Lacoste, G.D. Stancu, D.Z. Pai, and C.O. Laux, Journal of Physics D: Applied Physics 46 (2013) 464010
16. G.D. Stancu, F. Kaddouri, D.A. Lacoste and C.O. Laux, Journal of Physics D: Applied Physics 43 (2010) 124002
17. Z. Yin, A. Montello, C.D. Carter, W.R. Lempert, and I.V. Adamovich, Combustion and Flame, 160 (2013) 1594
18. D. Burnette, A. Montello, I.V. Adamovich, and W.R. Lempert, ”Nitric Oxide Kinetics in the Afterglow of a Diffuse Plasma Filament”, Plasma Sources Science and Technology, 23 (2014) 045007
19. Z. Yin, Z. Eckert, I.V. Adamovich, and W.R. Lempert, AIAA Paper 2014-1361, 52st AIAA Aerospace Sciences Meeting (SciTech 2014), 13-17 January 2014, National Harbor, MD, USA
20. L. Wu, J. Lane, N.P. Cernansky, D.L. Miller, A.A. Fridman, and A.Yu. Starikovskiy, Proceedings of the Combustion Institute 33 (2011) 3219
21. A. Starikovskiy, AIAA Paper 2012-0244, 50th AIAA Aerospace Sciences Meeting, January 2012, Nashville, TN, USA
22. V.V. Smirnov, O.M. Stelmakh, V.I. Fabelinsky, D.N. Kozlov, A.M. Starik, and N.S. Titova, Journal of Physics D: Applied Physics 41 (2008) 192001
23. T. Ombrello, S.H. Won, Y. Ju, and S. Williams, Combustion and Flame 157 (2010) 1906
24. T. Ombrello, S.H. Won, Y. Ju, and S. Williams, Combustion and Flame 157 (2010) 1916

25. N.A. Popov, *Plasma Sources Science and Technology* 20 (2011) 045002
26. M. Uddi, N. Jiang, E. Mintusov, I.V. Adamovich, and W.R. Lempert, *Proceedings of the Combustion Institute* 32 (2009) 929
27. Y. Zuzeek, I. Choi, M. Uddi, I.V. Adamovich, and W.R. Lempert, *Journal of Physics D: Applied Physics* 43 (2010) 124001
28. W. Sun, M. Uddi, S.H. Won, T. Ombrello, C. Carter, and Y. Ju, *Combustion and Flame* 159 (2012) 221
29. W. Sun, M. Uddi, T. Ombrello, S.H. Won, C. Carter, and Y. Ju, *Proceedings of the Combustion Institute* 33 (2012) 3211
30. C.K. Westbrook, *Annual Reviews of Physical Chemistry* 64 (2013) 201
31. J. Zador, C.A. Taatjes, and R.X. Fernandes, *Progress in Energy and Combustion Science* 37 (2011) 271
32. N. Tsolas, K. Togai, and R.A. Yetter, “Kinetics of Plasma Assisted Hydrocarbon Oxidation in Flow Reactors”, 53rd AIAA Aerospace Sciences Meeting (SciTech 2015), 5-9 January 2015, Kissimmee, FL
33. H. Wang, X. You, A.V. Joshi, S.G. Davis, A. Laskin, F. Egolfopoulos, and C.K. Law, USC Mech Version II. High-Temperature Combustion Reaction Model of H₂/CO/C₁-C₄ Compounds, http://ignis.usc.edu/USC_Mech_II.htm, May 2007
34. A. Konnov, Detailed Reaction Mechanism for Small Hydrocarbons Combustion, Release 0.5. <http://homepages.vub.ac.be/~akonnov/>, 2000
35. S. Nagaraja, V. Yang, and I. Adamovich, *Journal of Physics D: Applied Physics* 46 (2013) 155205
36. Z. Yin, I.V. Adamovich, and W.R. Lempert, *Proceedings of the Combustion Institute* 34 (2013) 3249
37. T. Li, I.V. Adamovich, and J.A. Sutton, AIAA Paper 2014-0664, 52nd AIAA Aerospace Sciences Meeting (SciTech 2014), 13-17 January 2014, National Harbor, MD
38. S. Nagaraja, T. Li, J. Sutton, I. Adamovich, and V. Yang, “Nanosecond plasma enhanced H₂/O₂/N₂ premixed flat flames”, accepted for publication in *Proceedings of the Combustion Institute*, 2014
39. G. Pilla, D. Galley, D.A. Lacoste, F. Lacas, D. Veynante, and C.O. Laux, *IEEE Transactions on Plasma Science* 34 (2006) 2471
40. M.S. Bak, S.-K. Im, M.G. Mungal, and M.A. Cappelli, *Combustion and Flame* 160 (2013) 2396
41. D.A. Lacoste, D.A. Xu, J.P. Moeck, and C.O. Laux, *Proceedings of the Combustion Institute* 34 (2013) 3259
42. B. Bohm, C. Heeger, R.L. Gordon, and A. Dreizler, “New Perspectives on Turbulent Combustion: Multi-Parameter High-Speed Planar Laser Diagnostics”, *Flow Turbulence and Combustion*, 86 (2011) 313-341

43. R.A. Patton, K.N. Gabet, N. Jiang, W.R. Lempert, and J.A. Sutton, *Applied Physics B: Lasers and Optics* 108 (2012) 377
44. K.N. Gabet, N. Jiang, W.R. Lempert, and J.A. Sutton, *Applied Physics B: Lasers and Optics* 101 (2010) 1
45. K.N. Gabet, R.A. Patton, N. Jiang, W.R. Lempert, and J.A. Sutton, *Applied Physics B: Lasers and Optics* 106 (2012) 569
46. N. Jiang, R.A. Patton, W.R. Lempert, and J.A. Sutton, *Proceedings of the Combustion Institute* 33 (2011) 767
47. H. Do, M.A. Cappelli, and M.G. Mungal, *Combustion and Flame* 157 (2010) 1783
48. H. Do, S.-K. Im, M. Cappelli, and M.G. Mungal, *Combustion and Flame* 157 (2010) 2298
49. K.V. Savelkin, D.A. Yarantsev, I.V. Adamovich, and S.B. Leonov, “Ignition and Flameholding in a Supersonic Combustor by an Electrical Discharge Combined with a Fuel Injector”, accepted for publication in *Combustion and Flame*, 2014
50. S.B. Leonov and D.A. Yarantsev, *Plasma Sources Science and Technology* 16 (2007) 132